The cooling of astrophysical media by HD

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ABSTRACT
The results of recent quantum mechanical calculations of cross-sections for rotational transitions within the vibrational ground state of HD are used to evaluate the rate of radiative energy loss from gas containing HD, in addition to H, He and H2. The cooling function for HD (i.e. the rate of cooling per HD molecule) is evaluated in steady state on a grid of values of the relevant parameters of the gas, namely the gas density and temperature, the atomic to molecular hydrogen abundance ratio and the ortho:para-H2 density ratio. The corresponding cooling function for H2, previously computed by Le Bourlot et al., is slightly revised to take account of transitions induced by collisions with ground-state ortho-H2 J=1.†: We then make a study of the rate of cooling of the primordial gas through collisions with H2 and HD molecules. In this case, radiative transitions induced by the cosmic background radiation field and, in the case of H2, collisional transitions induced by H+ ions should additionally be included.

Key words: molecular data – molecular processes – ISM: molecules – cosmology: miscellaneous.

1 INTRODUCTION
Le Bourlot, Pineau des Forêts & Flower (1999) computed the rate of cooling of astrophysical media by H2, incorporating the results of quantum mechanical calculations of cross-sections and rate coefficients for the collisional excitation of H2 by H, He and ground-state para-H2 (J=0). New collisional data have since become available (Roueff & Flower 1999; Roueff & Zeippen 1999; Flower 1999) which enable the contribution of HD to the cooling function to be reliably calculated, for the first time. Although the cosmic abundance of deuterium is low D/H < 10−5, the HD/H2 ratio can be enhanced by chemical fractionation, notably in the primordial gas, where the enhancement factor can attain 2 orders of magnitude (Puy et al. 1993; Galli & Palla 1998). Furthermore, the permanent dipole moment and lower rotational constant of HD favour cooling by HD, relative to H2, at high densities and low kinetic temperatures. It was desirable, therefore, to complement our recent calculation of the H2 cooling function by that of HD. We have additionally taken the opportunity to refine the H2 cooling function by incorporating collisional data relating explicitly to the excitation of ortho- and para-H2 by ground-state ortho-H2 (J=1) (Flower & Roueff 1999a).

Having assembled all the data necessary to compute the H2 and HD cooling functions, we make a case study of the contributions of these molecules to the cooling of the primordial gas. It is well known that trace amounts of H2 and HD are produced in the primordial gas, subsequent to the ‘freeze-out’ of H+ (see, for example, Black 1990; Stancil, Lepp & Dalgarno 1998). The fractional abundance of HD is calculated to be in the range 10−5–10−6, and that of HD only 2–3 orders of magnitude less, owing to chemical fractionation (Puy et al. 1993; Galli & Palla 1998). Although small compared with the cooling associated with the adiabatic expansion of the Universe, the cooling of the gas by H2 and HD is expected to play an important, perhaps a crucial, role in the formation of condensations, triggered by thermal and gravitational instabilities.

In the following Section 2, we update the collisional data for H2 and summarize those that are now available for HD; the calculation of the cooling function is outlined. We consider the application of the results to the primordial gas in Section 3. In this context, it is essential to include radiative transitions induced by the cosmic background radiation. In the case of H2, collisional transitions induced by protons are found to be important. Our concluding remarks are made in Section 4.

2 COLLISIONAL DATA AND COOLING FUNCTIONS

2.1 Rate coefficients
The status of computations of collision cross-sections relating to...
the excitation of H$_2$ by H, He and para-H$_2$ ($J = 0$) was reviewed by Le Bourlot et al. (1999). Quantum mechanical calculations of cross-sections, and then thermally averaged rate coefficients, for the excitation of ortho- and para-H$_2$ by ground-state ortho-H$_2$ ($J = 1$) have since been completed (Flower & Roueff 1999a), for all rovibrational levels of H$_2$ up to approximately 18 000 K above the ground state. These additional rate coefficients are now available from the CCP7 website (http://ccp7.dur.ac.uk/) or directly from the authors. As previously, we have used a three-parameter fit to the temperature dependence of the rate coefficients, of the form

$$\log [q(\sigma J \rightarrow \sigma' J')] \text{cm}^3 \text{s}^{-1} = a + b/t + c/t^2,$$

where $t = [T(\text{K})/10^3] + \delta t$, and $\delta t$ is a constant value (in practice, $\delta t = 1.0$ for transitions of H$_2$) which prevents divergence of the rate coefficients as $t \rightarrow 0$. The values of the fit parameters are given for de-excitation transitions; those for excitation should be obtained from detailed balance.

We have made the analogous fits to the rate coefficients for the de-excitation of HD by H ($\delta t = 2/3$), He ($\delta t = 1/3$), and ortho- and para-H$_2$ ($\delta t = 1/2$); these data are now available from http://ccp7.dur.ac.uk/. All the rotational levels of HD that lie below the first vibrationally excited state have been considered, i.e. up to $v = 0$, $J = 8$ at 4445 K above the $J = 0$ ground state; $v = 0$, $J = 9$ was additionally included in the HD–H and HD–He calculations. We have already noted that cooling by HD is significant, relative to that by H$_2$, only at low temperatures.

Important differences between collisions involving H$_2$ and those involving HD arise from the shift of the centre of mass of the HD molecule from the mid-point of the internuclear line. Although the interaction potentials for HD–X (X = H, He, H$_2$) are the same as for H$_2$–X, these potentials are not symmetric with respect to the centre of mass of the HD molecule. It follows that transitions $\Delta J = 1$, forbidden in non-reactive scattering on H$_2$, are allowed in HD. Indeed, such transitions dominate the inelastic scattering process. Whilst this lack of symmetry renders the cross-section calculations for HD more computationally onerous than for H$_2$, where the ortho- and para-forms can be treated separately, it also improves the reliability of the HD cooling function, relative to that of H$_2$. The reason is that, in the case of H$_2$–H collisions, rotational population transfer at low temperatures occurs principally through $\Delta J = 2$ transitions, for which the rate coefficients are very small and sensitive to the residual uncertainties in the interaction potential, and to the form of the ground-state vibrational eigenfunction; these effects are much less important in the case of HD–H collisions (Flower & Roueff 1999b).

### 2.2 Cooling functions

We have recomputed the rate of cooling per H$_2$ molecule, $W(\text{H}_2) \text{erg s}^{-1}$, for the grid of values of $n_H = n(\text{H}) + 2n(\text{H}_2)$, $T$, $n(\text{H})/n(\text{H}_2)$, and $n(\text{ortho})/n(\text{para})$ specified by Le Bourlot et al. (1999), namely

$$1 \leq n_H \leq 10^6 \text{cm}^{-3},$$

$$100 \leq T \leq 10^4 \text{K},$$

$$10^{-8} \leq n(\text{H})/n(\text{H}_2) \leq 10^6,$$

$$0.1 \leq n(\text{ortho})/n(\text{para}) \leq 3,$$

$$n(\text{He})/n(\text{H}) = 0.10.$$

In the present calculations, spontaneous radiative transitions and transitions induced by collisions with H, He, and both para-H$_2$ ($J = 0$) and ortho-H$_2$ ($J = 1$) have been included. As compared with our previous calculations (Le Bourlot et al. 1999), the inclusion of population transfer in collisions with ortho-H$_2$ ($J = 1$) gives rise to only modest changes in the cooling function, for simultaneously small values of $n_H$ and $T$. This revised cooling function is available from http://ccp7.dur.ac.uk/, but the changes are sufficiently small that the plots of $W(\text{HD})$ below may be sensibly compared with the corresponding plots of $W(\text{H}_2)$ given by Le Bourlot et al. (1999).

We have computed the rate of cooling per HD molecule, $W(\text{HD})$, on a grid of values of the four independent parameters, in the ranges

$$1 \leq n_H \leq 10^8 \text{cm}^{-3},$$

$$30 \leq T \leq 3 \times 10^3 \text{K},$$

$$10^{-4} \leq n(\text{H})/n(\text{H}_2) \leq 10^7,$$

$$0.1 \leq n(\text{ortho})/n(\text{para}) \leq 3.$$

The abundance ratio $n(\text{He})/n(\text{H})$ was again set equal to 0.10. For each set of values of these parameters, the populations of all the levels $v = 0$, $J = 8$ of HD were calculated, allowing for collisional excitation and de-excitation by He, H, and ortho- and para-H$_2$, and for spontaneous radiative decay. The cooling function (rate of cooling per HD molecule) is defined as

$$W(\text{HD}) = \frac{1}{n(\text{HD})} \sum_{\epsilon_1, \epsilon_2, J_1, J_2} (E_{\epsilon_1} - E_{\epsilon_2}) n_{\epsilon_1} A(\epsilon_1 J_1 \rightarrow \epsilon_2 J_2),$$

and is given in erg s$^{-1}$ ($=10^{-7}$ W). Steady state ($dn_{\epsilon_1}/dt = 0$) was assumed throughout, and, as noted above, $v = v' = 0$, $J \leq 8$. The function $W(\text{HD})$ is independent of the density of HD molecules, $n(\text{HD})$.

Flower (1999) has shown that the rate coefficients for collisional transfer in HD, induced by collisions with H$_2$ molecules, are insensitive to the rotational state of the perturber. Fig. 1 shows that para-H$_2$ ($J = 0$) and ortho-H$_2$ ($J = 1$) yield very similar results for the rate coefficient of the $J = 1 \rightarrow 0$ transition in HD, for example. It follows that the cooling function $W(\text{HD})$ is almost independent of the ortho:para density ratio. Furthermore, it turns out that $W(\text{HD})$ is insensitive to the H/H$_2$ density ratio, as
may be seen from Fig. 2. Although the rate coefficients for rotational population transfer in HD–H \(_2\) scattering are typically twice as large as in HD–H collisions (compare Fig. 1), the number density of H\(_2\), \(n(H_2)\), \(<\) \(n_H/2\) when \(n(H)\). It follows that, for a given value of \(n_H\), the cooling function is only weakly dependent on the H/H\(_2\) abundance ratio. Essentially, \(W(HD)\) is a function of \(n_H\) and \(T\) only, and we have fitted the numerical results to an appropriate and compact function, \(W(HD; n_H, T)\), which we supply as a fortran routine \(W-HD.f\).

Within the specified ranges, this fit is good to about 10 per cent, with slight deterioration towards the simultaneously highest values of \(T\) and \(n_H\).

Fig. 3 illustrates the variations of the HD cooling function with \(n_H\) and \(T\), within the ranges specified above. As the rotational level populations approach a Boltzmann distribution \((n_H > 10^3 \text{ cm}^{-3})\), \(W\) becomes independent of the gas density, \(n_H\). The approach of \(W\) to its value in local thermodynamic equilibrium is shown in Fig. 4. The density required for \(W_{\text{LTE}}\) to obtain is higher in the case of HD than in the case of H\(_2\), at least at low temperatures. The probabilities of the electric dipole \((J \rightarrow J - 2)\) transitions in HD are much larger than the corresponding electric quadrupole \((J \rightarrow J - 1)\) probabilities in H\(_2\), particularly for transitions between the lower levels. On the other hand, the rate coefficients for collisional transfer between these levels are also larger in the case of HD, and some compensation occurs. In Table 1, we list the critical densities at which the probabilities (s\(^{-1}\)) of spontaneous radiative transitions out of rotational levels \(J\) of HD are equal to the probabilities of collisional de-excitation by ortho-H\(_2\) at \(T = 100\) K (for the purposes of illustration). Critical densities for rovibrational transitions in H\(_2\) are given by Le Bourlot et al. (1999, table 1).

3 COOLING OF THE PRIMORDIAL GAS

3.1 H\(_2\)

In the primordial gas, \(n(H) \gg n(H_2)\) and the value of \(W(H_2)\) is dependent on \(n(H)\) and \(n(He)\) but independent of \(n(H_2)\). As we show below, the fractional abundance of protons is sufficiently high for H\(_2\)--H\(^+\) collisions to be important, perhaps dominant.

Figure 2. The cooling function, \(W(HD)\) (in units of \(10^{-7} \text{W}\)), calculated for \(n_H = 10^2\) and \(10^3 \text{ cm}^{-3}\) and an ortho:para-H\(_2\) density ratio of 1. The full curves refer to an H/H\(_2\) abundance ratio of \(10^{-4}\), and the dot–dashed curves to a ratio of \(10^4\). The corresponding plot of \(W(H_2)\) is given by Le Bourlot et al. (1999, fig. 6a).

Figure 3. The cooling function, \(W(HD)\) (in units of \(10^{-7} \text{W}\)), calculated for \(1 \leq n_H = 10^4 \text{ cm}^{-3}\), an ortho:para-H\(_2\) density ratio of 1, and an H/H\(_2\) abundance ratio of 1. The corresponding plot of \(W(H_2)\) is given by Le Bourlot et al. (1999, fig. 4b).
collisions with H atoms and spontaneous radiative transitions into account; we now compare $W(H_2)$ with the results of the calculations of these authors.

In Fig. 5, our cooling function $W(H_2)$ is plotted as a function of the kinetic temperature, $T$, for $n(H) = 1$ and $10^6$ cm$^{-3}$, $n(H_2)/n(H_2) = 10^5$, and $n(\text{ortho})/n(\text{para}) = 3$. Comparison is made with the ‘low’- and the ‘high’- density results of Tiné et al. (1998) and Galli & Palla (1998). Both these groups of authors used quantum mechanical calculations (Forrey, Balakrishnan & Dalgarno 1997) of $H_2$-H rotational excitation cross-sections at low temperatures, and semi-classical calculations at high temperatures.

Fig. 5 shows that all three evaluations of the cooling function agree well at low temperatures ($T \approx 1000$ K), at both low and high densities. At low densities, this apparent agreement is partly fortuitous, as our own calculations additionally include the contribution of $H_2$-He collisions. Although He is 10 times less abundant than H, its contribution to the total rate of excitation of $H_2$ at $T = 100$ K is comparable to that of H (Le Bourlot et al. 1999). For $T > 1000$ K, our results lie below those of Tiné et al. and Galli & Palla, especially at low densities. This discrepancy arises from the different approaches to the collision problem (semi-classical, as opposed to quantum mechanical) and determinations of the reactive scattering contributions to the rate coefficients (cf. Le Bourlot et al. 1999). However, cosmological models (Puy et al. 1993; Galli & Palla 1998) show that significant amounts of $H_2$ are present only for redshifts $z < 400$, and so the
i.e. the rate of heating exceeds the rate of cooling, as anticipated. At low temperatures and densities, cooling is determined principally by the $J = 0 \rightarrow 2$ transition in para-H$_2$, and

$$\Lambda \approx \Lambda_{20} = \sum_p n_p n_0 d_p^{(0)}(T)(E_2 - E_0).$$

Furthermore, if $T_e \ll T_{20}$, the ground-state population density $n_0 = n_{\text{para-H}_2}$, and so

$$\Lambda \approx n_{\text{para-H}_2} \sum_p n_p d_p^{(0)}(T)(E_2 - E_0).$$

In the limit of low densities and temperatures, the cooling function $W(H_2)$, defined analogously to that in Section 2 above and evaluated neglecting induced radiative transitions, is such that

$$n(H_2)W(H_2) \approx n_oA(2 \rightarrow 0)(E_2 - E_0)$$

$$\approx \sum_p n_p n_0 d_p^{(0)}(T)(E_2 - E_0)$$

$$\approx n_{\text{para-H}_2} \sum_p n_p d_p^{(0)}(T)(E_2 - E_0) = \Lambda,$$

where the subscripts refer to the values of the rotational quantum number $J$ in the vibrational ground state. Thus, in this limit, the rate of cooling, $\Lambda$, of the primordial gas is determined by the cooling function, $W$. In general, this is not the case, and the heating and cooling rates should be determined from equation (2), allowing for both spontaneous and induced radiative transitions and for collisions (using the fits that are provided to the temperature dependence of the rate coefficients: see Section 2 above).

The cooling functions calculated by Tine et al. (1998) and Galli & Palla (1998) incorporated the contributions of collisions with H atoms only. Galli & Palla (1998) noted the possible importance of reactive collisions of H$_2$ with H$^+$, but neglected such collisions in their calculations of the cooling function. Rate coefficients for rotational transitions occurring in reactive collisions of H$_2$ with H$^+$ have been determined by Gerlich (1990). The rate coefficients for rotational de-excitation of H$_2$ by H$^+$ (which may involve $\Delta J = 1$ as well as $\Delta J > 1$) are in the range $10^{-10} - 10^{-9}$ cm$^3$ s$^{-1}$, almost independent of the kinetic temperature, and much larger than the rate coefficients for de-excitation by H and He at low temperatures. Adopting the fractional ionization $n(H^+)/n(H) \approx 3 \times 10^{-4}$ computed, subsequent to freeze-out, by Galli & Palla (1998), we obtain a rate of de-excitation of H$_2$ by H$^+$ which is of the order of $10^{-13}n(H)$ s$^{-1}$; this is of the same order as the rate of collisional de-excitation of the $J = 2$ level of H$_2$ by H atoms at $T = 100K$. As shown by Flower & Pineau des Forêts (2000), the rate of heating of the primordial gas that is computed by including population transfer induced by collisions with protons is substantially greater than the rate of heating obtained by neglecting this process.

The calculations of the H$_2$ rovibrational level populations are time-dependent. As noted by Le Bourlot et al. (1999), two-timescales characterize such calculations: that for thermalization of the level populations of ortho- and para-H$_2$ separately; and that for establishing equilibrium between ortho- and para-H$_2$, through reactive collisions. In the case of the primordial gas, where, as we have seen, population transfer is governed by collisions with H$^+$, these two timescales become comparable. By running the calculation to a sufficiently large time (which must remain less than the expansion time-scale), the steady-state values of the heating and cooling functions can be derived.

3.2 HD

In Fig. 6, we compare $W(\text{HD})$, computed for $n_H = 1$ cm$^{-3}$, an ortho:para-H$_2$ density ratio of 0 (pure para-H$_2$), and an H/He abundance ratio of $10^4$, with the values that derive from fig. A2 of Galli & Palla (1998). The agreement between these two determinations of the HD cooling function may be seen to be satisfactory. Galli & Palla (1998) obtained the HD–H rate coefficients by scaling the HD–He rate coefficients of Schaefer (1990) by a factor of 1/1.27. Roueff & Flower (1999) have since shown that the HD–H rate coefficients tend to be somewhat larger for de-excitation transitions $\Delta J = 1$ (but smaller for $\Delta J = 2$) than in the case of HD–He, which probably accounts for the fact that our values of $W(\text{HD})$ exceed those of Galli & Palla (1998). Owing to the much larger values of the rate coefficients for HD–H collisions, as compared with those for H$_2$–H, collisions with H$^+$ are not significant in rotational population transfer in HD.

4 CONCLUDING REMARKS

In this paper, the data required to compute the contribution of HD to the overall rate of cooling of astrophysical media have been supplied, and we have completed the data set necessary to compute the cooling by H$_2$ molecules. The cooling functions, $W(H_2)$ and $W(\text{HD})$, have been calculated, neglecting induced radiative transitions, on a grid of values of the following parameters: the gas density, $n_H$; the kinetic temperature; the atomic to molecular hydrogen density ratio, $n(H)/n(H_2)$; and the ortho- to para-H$_2$ ratio, $n(\text{ortho})/n(\text{para})$. $W(\text{HD})$ is found to be only weakly dependent on both $n(H)/n(H_2)$ and $n(\text{ortho})/n(\text{para})$, and a compact functional dependence on $n_H$ and $T$ has been derived.

We have made a study of the contribution of H$_2$ and HD to the cooling of the primordial gas. Because of the greater efficiency of protons, relative to H atoms, in inducing rotational transitions in H$_2$, it is the former that tend to govern population transfer between the rotational levels of this molecule. As proton collisions can, even at low temperatures, induce transitions in which $\Delta J$ is not only even but also odd, thereby interchanging the ortho- and para-modifications of H$_2$, the time-scale for establishing steady-state populations within each modification is of the same order as the
time-scale for establishing the equilibrium ortho:para ratio. As shown by previous authors, the net effect of collisions with H\(_2\) molecules is to heat, rather than to cool, the gas, beyond the time at which matter and radiation decouple and the kinetic temperature falls below the background radiation temperature. In practice, the level populations are close to being thermalized at the (blackbody) radiation temperature; collisional processes represent departures from local thermodynamic equilibrium.

The cooling function for HD is found to be in good agreement with that derived by Galli & Palla (1998). Rate coefficients for rotational transitions within the vibrational ground state of HD, induced by H atoms, are much larger than for the corresponding transitions in H\(_2\). Consequently, proton collisions contribute insignificantly to population transfer in the HD molecule.

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